

**EFFECT OF LIGNITE PROPERTIES AND ASH CONSTITUENTS
ON THE HYDROLIQUEFACTION BEHAVIOR OF THE TURKISH LIGNITES**

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INTRODUCTION

In Turkey, coal represents major non-renewable energy resources since lignite and bituminous coal reserves are known to be around 8.1 billion tons and 1.4 billion tons, respectively. The high demand for imported fuel oil for energy requirement of Turkey has led to strong and sustained interest in the prospects for producing liquids from the coal resources. Due to the high sulfur (1-5 %), ash (10-50 %), moisture (10-40%) and low calorific value of Turkish lignites, coal liquefaction processes is believed to be one of the efficient way by converting them to clean liquid fuels and chemical feedstocks.

The purpose of this study was to develop correlations between physical, chemical and petrographic properties of representative Turkish lignites and liquefaction yield data obtained in tetralin, anthracene, creosote and vacuum residue oils, with or without catalyst, at 440 °C and 80 bar hydrogen pressure (cold charge).

EXPERIMENTAL

Materials and Procedure

Experiments were carried out by BE (Beypazari), CA (Can), EL (Elbistan), IL (Ilgin), KN (Kangal), KR (Karliova), SA (Saray), SE (Seyitomer), SO (Soma), TU (Tuncbilek), YA (Yatagan) lignites using tetralin, Tupras vacuum residue oil, anthracene and creosote oils as solvents. Creosote and anthracene oils used in this study were obtained from Karabuk Demir Celik Fabrikalari A.S. and vacuum residual oil (VR) was provided by Tupras, Turkey. Tetralin was supplied by Merck company and it was used as received. The creosote oil used has a carbon to hydrogen ratio of 1.24 (90.78% C, 6.12% H, and 0.70% N); anthracene oil has a carbon to hydrogen ratio of 1.27 (91.50% C, 6.01% H, and 0.75% N); vacuum residue oil has a carbon to hydrogen ratio of 0.64 (85.58% C, 11.06% H and 0.50% N). Two catalysts were used in these experiments. A commercially available alumina supported CoMo (3% CoO and 10% MoO₃ on Al₂O₃) was used in extrusion form having 2.6-3 mm diameter and bulk density of 0.5-0.6 kg/lit. In addition, a disposable catalyst, red mud (15.03% SiO₂, 35.96% Fe₂O₃, 21.04% Al₂O₃, 4.56% TiO₂, 9.3% Na₂O and 3.5% CaO) received as a waste by-product of Seydisehir Aluminum Company, having a grain size of 0.01 mm, was used. The elemental analysis for carbon, hydrogen and nitrogen was done by Beller Microanalysis Laboratories in Germany. The ash samples prepared at 800 °C were analyzed with Inducted Coupled Plasma (ICP) Leeman, Model PS1000 series.

The liquefaction experiments were carried out in a 250 ml magnetically stirred and electrically heated stainless steel autoclave manufactured by Ernst Haage. Based on the literature and evaluation of our previous work, the reaction temperature, pressure and reaction time for these experiments were chosen as 440 °C, 80 bar hydrogen (cold charge), respectively (1-3). Solvent/lignite or asphaltite ratio was chosen as 2 (db). At the completion of a liquefaction experiment, the autoclave was cooled overnight to room temperature and the gases were analyzed by Shimadzu Moduline GC-9A model gas chromatography. The liquid products and solid residue washed from the autoclave with toluene and fractionated by Soxhlet extraction into oil (hexane soluble

material); asphaltene (toluene soluble, hexane insoluble material); preasphaltene (tetrahydrofuran (THF) soluble, toluene insoluble material); and residue (THF insoluble material). The blank runs for all sets of experiments with no lignite present were carried out with all solvents to evaluate the reactivity of the lignite samples.

RESULTS AND DISCUSSION

The complete experimental data were reported in previous work (1-3). The characterization data for the lignites used are given in Tables 1 and 3. The experimental data used in this study are given in Figures 1-2.

The intercorrelation of experimental results and lignite characteristics was evaluated by simple linear regression analysis using Microstat Statistical Package program. By the application of simple linear regression, it was found that generally a good correlation did not exist between individual lignite properties and yield and conversion data. Only total sulfur content and xylene extract of lignites were observed to give partially acceptable correlations for the oil yields. The correlation coefficient of experiments using tetralin as solvent is as follows:

$$O (\% \text{ daf}) = 3.10 S_t + 50.84$$

$$R^2 = 0.7024 ; \text{SEOE}(\text{standard error of estimation}) = 4.45$$

The oil yields obtained in experiments using creosote oil and red mud catalyst were correlated with xylene extract content of lignites by the following regression equation

$$O (\% \text{ daf}) = 1.980 \text{ XEL} + 29.39$$

$$R^2 = 0.560 ; \text{SEOE} = 6.68$$

The effect of individual coal properties are not easily assessed as noted above. This is primarily due to the fact that the individual properties being highly cross-correlated hence they could not be independently varied. Therefore, the multiple regression analysis was employed and in order to improve the correlation coefficients unfitting lignites were eliminated. The equations developed with oil yield as the dependant variable are given in Table 4. The correlation coefficients indicated that a relationship existed between carbon, total sulfur and forms of sulfur, volatile matter, huminite plus exinite, and xylene extract of lignites with the oil yields obtained by using four different solvents and two different catalysts. The highest correlation coefficient was obtained for experimental data using creosote oil as the solvent. For this case three equations were derived, using the pyritic sulfur, total sulfur and organic sulfur contents of the lignites. The R^2 values are 0.6819, 0.9727 and 0.7643 for S_p , S_t and S_o , respectively as shown in Equations 2-4. It is commonly believed that one of the factors contributing to the liquefaction yield is promotion by sulfur. However, the exact role of sulfur is not well understood. The organic sulfur is presumably present in coal as mercaptans, sulfides, thioethers. It is expected that thioethers are thermally cleaved at considerably low temperature to produce active coal fragments during the liquefaction reactions (4). Several workers have shown that conversion of coals of low sulfur content can be increased by from 5 to 18 percent through the addition of pyrite (5,6). It has been observed that during liquefaction, pyrite is reduced to pyrrhotite and hydrogen sulfide at roughly the same rate as the organic matter is converted to liquid products. Thus coals containing high proportions of pyritic sulfur will tend to form pyrrhotites with a high level of iron vacancies, which appear to promote liquefaction.

There is an indication that an increase in ash, huminite plus exinite, xylene extract and volatile matter contents of lignites help the hydrol liquefaction process positively. On the other hand, as the negative coefficient before the elemental carbon content in Eq.5 indicates, increasing the elemental carbon content decreases the oil yield. As shown in equations 2-4 and 6-7, correlations were obtained when HU and

HU+EX contents of the lignite were used as the petrographic correlating parameter. The work undertaken by Given and coworkers in batch reactor showed that some coal macerals, including vitrinite, pseudovitrinite and liptinites are reactive while inertinite, as its name implies, is inert in coal liquefaction (7). The trend for increasing reactivity with increasing volatile matter content as given in Equations 2-4 was expected as volatile matter is known to be thermally easily liberated. Given also found that volatile matter had a direct correlation with conversion at 60 minutes and exhibited the highest correlation coefficient among the coal properties investigated (7). The oil yield increases as the xylene extract content of the lignite increases, as seen in Equations 1-4 and 7-8. The high partial correlation coefficients for xylene extract in Equations 2-4 indicate that it may be considered as a good correlation parameter for liquefaction reactions.

The equations 1, 6 and 8 show that increased ash content increases oil yield. It is known that the high ash coals are more easily hydrogenated than low ash coals because certain coal ash minerals catalyze the reactions (8-9). The observed relation between ash and oil yield data was further evaluated with respect to concentrations of ash constituents (g/100g of inorganic matter). In this study total Fe, Al, Si, Mg, Ca, Na and K concentrations were chosen as the independent variable, since the active form of the minerals has not been ascertained. There appears to be direct correlation between oil yield with Fe constituents but the dependence is not marked. The yield of oil data shows a tendency to increase with increasing Al, Ca and Mg content though with more scatter than in the case of Fe content. No detectable trends were observed with Si contents of ash. In this study, an examination of oil data for all samples studied did not reveal any statistically significant correlations with Na and K content of the ash. We have not included in this paper a thorough discussion for the effects of ash constituents on liquefaction yields because we are carrying out a detailed multiple regression analysis on that topic.

CONCLUSIONS

In this study, the oil yields of the Turkish lignites under same hydroliquefaction conditions in the presence of tetralin, creosote, anthracene and vacuum residue oils using a catalyst or not, were correlated total, pyritic and organic sulfur, volatile matter, elemental carbon, huminite, huminite plus exinite, xylene extract, ash and ash constituents of lignites using simple and multiple linear regression analysis. The derived equations indicated that although use of different lignite, solvents and catalyst resulted in different yield data, the oil yields exhibit almost similar dependencies on lignite characteristics. However, it should be noted that in order to strengthen the validity of these equations, the number of lignite sample studied should be increased. In any case, much more has to be done in order to correlate the liquefaction data with lignite properties.

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Table I
Analytical Data for Lignites Used

Lignite Sample	C (%daf)	H (%daf)	N (%daf)	S _t (%dry)	S _p (%dry)	S _o (%dry)	S _g (%dry)	VM (%daf)	FC (%daf)	ash (%dry)	H/C (Atomic)	XEL (%daf)
BE	64.90	5.61	2.19	5.69	2.88	2.33	0.48	35.61	64.38	49.88	1.04	3.83
CA	66.38	4.82	1.67	4.23	0.90	2.44	0.89	37.53	62.47	27.15	0.87	1.34
EL	63.95	4.97	2.48	5.82	3.33	2.22	0.27	54.78	45.22	28.19	0.90	5.04
IL	68.19	5.11	1.27	2.95	1.12	1.45	0.38	40.32	59.68	33.61	0.90	5.69
KN	67.66	4.52	2.78	5.63	3.15	1.93	0.55	62.93	37.07	38.50	0.80	5.22
KR	66.97	5.55	2.09	0.79	0.40	0.30	0.09	49.43	50.57	49.20	0.99	4.31
SA	61.32	4.73	1.60	4.97	0.15	1.25	3.57	48.21	51.79	59.99	0.93	12.62
SE	71.97	4.70	2.32	1.45	0.26	1.02	0.17	48.65	51.35	24.87	0.78	10.30
SO	64.10	5.62	1.47	0.80	0.41	0.34	0.05	39.69	60.30	55.51	1.05	2.02
TU	78.30	5.65	3.03	1.37	0.64	0.67	0.06	31.59	68.41	18.59	0.87	0.95
YA	63.65	4.87	1.59	5.11	1.72	2.98	0.41	44.41	55.59	25.35	0.92	6.90

BE: Beypazari; CA: Can; EL: Elbistan; IL: Ilgin; KN: Kangal; KR: Karliova; SA: Saray; SE: Seyitomer; SO: Soma; TU: Tuncbilek; YA: Yatagan; S: total sulfur; S_p: pyritic sulfur; S_g: organic sulfur; S_o: sulfatic sulfur; VM: volatile matter; FC: fixed carbon; daf: dry-ash-free; XEL: Xylene extract of lignites.

Table II
Maceral Group Analysis of Lignites

Lignite	Maceral Group Analysis (volume %)					Organic Based Maceral Group Analysis (volume %)		
	Huminites (HU)	Exinites (EX)	Inertinites (IN)	Pyrites	Clays	Huminites (HU)	Exinites (EX)	Inertinites (IN)
BE	77	6	4	3	10	88	7	5
CA	74	6	4	4	12	88	7	5
EL	69	5	11	3	12	81	6	13
IL	70	7	9	3	11	81	8	11
KN	54	4	7	3	32	83	6	11
KR	52	5	7	2	34	81	8	11
SA	71	6	7	2	14	85	7	8
SE	77	7	8	2	6	84	8	8
SO	62	3	9	2	24	84	4	12
TU	80	8	6	1	5	85	9	6
YA	77	6	5	4	8	88	7	5

Table III
Chemical Analysis of Ash (g/100 g organic matter)

Lignite	Si	Fe	Al	Mg	Ca	K	Na
BE	22.06	6.70	6.60	2.59	6.89	1.14	3.54
CA	8.24	3.26	5.55	0.13	1.18	0.27	0.12
EL	5.47	1.45	2.69	0.74	6.87	0.20	0.12
IL	9.36	2.88	6.88	0.96	3.75	1.60	2.06
KN	11.35	1.69	7.20	0.84	8.64	0.52	0.29
KR	33.26	3.70	3.97	0.81	2.34	2.44	0.42
SA	32.55	14.42	18.19	4.03	5.49	2.88	0.40
SE	9.02	6.87	1.94	1.12	2.18	0.13	0.34
SO	27.65	3.64	17.80	1.07	8.05	1.50	0.46
TU	5.48	2.29	3.52	0.47	0.37	0.27	0.03
YA	4.30	3.28	2.97	0.54	4.23	0.25	0.07

Table IV

Relations Between Oil Yield and Various Properties of Turkish Lignites

Solvent + Catalyst Used	Excluded Lignite	Derived Equation	Eq (1) SEOE = 5.74
A.O.	SE, BE	$O (\% \text{daf}) = 20 + 0.44 \text{ ash} + 1.17 \text{ XEL}$ $R^2 = 0.7719$ $R^2_{\text{ash}} = 0.5598$ $R^2_{\text{XEL}} = 0.3501$	Eq (1) SEOE = 5.74
C.O.	SO, TU	$O (\% \text{daf}) = -247.4 + 1.41 S_p + 0.18 \text{ VM} + 2.00 \text{ XEL} + 2.93 (\text{HU} + \text{EX})$ $R^2 = 0.9890$ $R^2_{S_p} = 0.6819$ $R^2_{\text{VM}} = 0.4644$ $R^2_{\text{XEL}} = 0.9890$ $R^2_{(\text{HU} + \text{EX})} = 0.6819$	Eq (2) SEOE = 1.36
		$O (\% \text{daf}) = -223.1 + 0.99 S_p + 0.17 \text{ VM} + 1.79 \text{ XEL} + 2.66 (\text{HU} + \text{EX})$ $R^2 = 0.9991$ $R^2_{S_p} = 0.9727$ $R^2_{\text{VM}} = 0.9079$ $R^2_{\text{XEL}} = 0.9977$ $R^2_{(\text{HU} + \text{EX})} = 0.9967$	Eq (3) SEOE = 0.40
		$O (\% \text{daf}) = -216.1 + 2.32 S_p + 0.20 \text{ VM} + 1.89 \text{ XEL} + 2.56 (\text{HU} + \text{EX})$ $R^2 = 0.9918$ $R^2_{S_p} = 0.7643$ $R^2_{\text{XEL}} = 0.9800$ $R^2_{(\text{HU} + \text{EX})} = 0.9645$	Eq (4) SEOE = 1.17
TET	EL, SO	$O (\% \text{daf}) = 125.1 - 0.97 C + 1.82 S_p$ $R^2 = 0.9039$ $R^2_C = 0.8697$ $R^2_{S_p} = 0.5382$	Eq (5) SEOE = 2.12
VR	BE, KN	$O (\% \text{daf}) = 29.22 + 0.09 \text{ Ash} + 0.30 \text{ HU}$ $R^2 = 0.4800$ $R^2_{\text{ash}} = 0.4169$ $R^2_{\text{HU}} = 0.3999$	Eq (6) SEOE = 1.61
C.O. + CoMo	KR, KN	$O (\% \text{daf}) = -61.62 - 1.22 \text{ XEL} + 1.18 (\text{HU} + \text{EX})$ $R^2 = 0.5704$ $R^2_{\text{XEL}} = 0.4904$ $R^2_{(\text{HU} + \text{EX})} = 0.3512$	Eq (7) SEOE = 5.70
C.O. + Red Mud	KR	$O (\% \text{daf}) = 25.25 + 0.20 \text{ Ash} + 1.67 \text{ XEL}$ $R^2 = 0.7908$ $R^2_{\text{ash}} = 0.3286$ $R^2_{\text{XEL}} = 0.7091$	Eq (8) SEOE = 4.42

A.O.: Anthracene oil; C.O.: Creosote oil; TET: Tetralin; VR: Vacuum residue; CoMo: Cobalt Molybdenum catalyst.

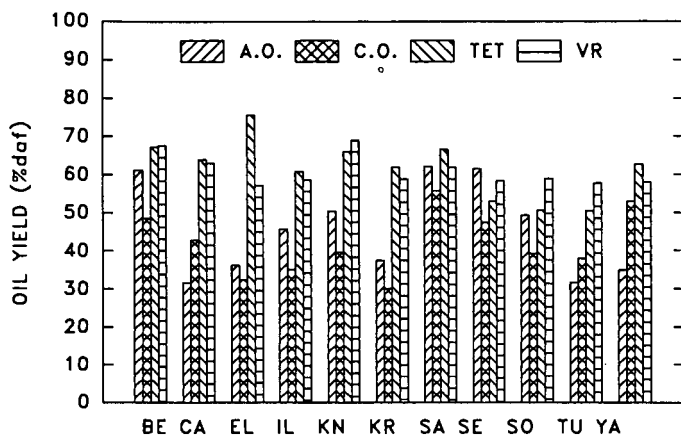


Figure 1. Effect of solvents on the oil yields of Turkish lignites; P = 80 bar (H₂, cold charge), T = 440 °C, reaction time = 1 hr.

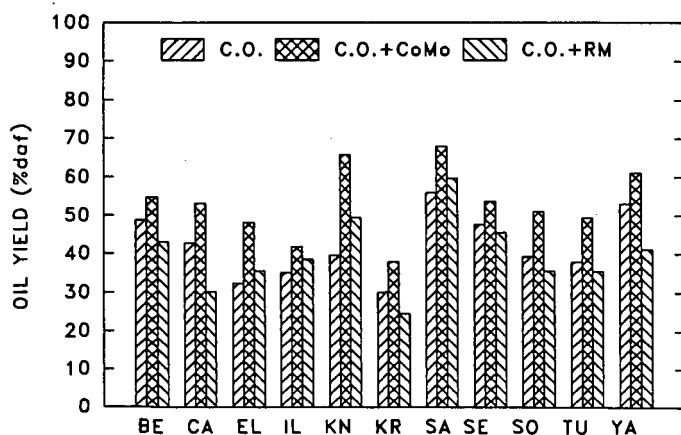


Figure 2. Effect of catalysts on oil yields of Turkish lignites; P = 80 bar (H₂, cold charge), T = 440 °C, reaction time = 1 hr.